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It is certified that the work contained in the thesis titled " ***Heterocyclic Compounds as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution***" by "***Chandrabhan Verma***" has been carried out under my supervision and that this work has not been submitted elsewhere for a degree. It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. Degree.

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# DECLARATION BY THE CANDIDATE

I, "***Chandrabhan Verma***", certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of "Prof. ***M.A. Quraishi***" from "July-2012" to “Sept-2016”, at the "*Department of Chemistry*", Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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It is certified that the above statement made by the student is correct to the best of my/our knowledge.


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# ACKNOWLEDGEMENTS

*This thesis, the conclusion of several years' work, is a result that I could not have achieved without the support of many peoples to whom I would like to express my gratitude.*

*Foremost I would like to express my gratitude towards my supervisor Prof. M. A. Quraishi, Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi, for his constant guidance, valuable suggestions and kind encouragement during my association with his research group. I am thankful to Prof. (Mrs.) R. B. Rastogi, Head, Department of Chemistry, Indian Institute of technology, Banaras Hindu University, Varanasi. for providing necessary facilities during my research work.*

*My special thanks to all my RPC members, Prof. S. H. Hasan, Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi and Prof. Om Prakash Department of Ceramic Engineering , Indian Institute of Technology, Banaras Hindu University, Varanasi for their constant guidance, valuable suggestions and kind encouragement during my research work.*

*I am gratefully acknowledging the facilities provided by the Department of Metallurgical Engineering, Indian Institute of technology, Banaras Hindu University, Varanasi.*

*I have deep sense of gratitude for all Teachers of the Department of Chemistry, Indian Institute of technology, Banaras Hindu University, Varanasi for their cooperation and inspiration.*

*I am obliged to all my seniors and friends; Dr. Ishtiaque Ahamad, Dr. Deelip Kumar Yadav, Dr. Sudheer, Dr. Chitrasen Gupta, Dr. Ambrish Singh, Dr. Dheeraj Singh Chauhan, Mr. Kashif Rahmani Ansari, Mrs. Priyanka Singh, Md. Javed and Parvez Akhtar, Kritika Srivastava and Jiyaul Haque for their vital contributions in my research work.*

*I would like to acknowledge my indebtedness to my parents Mr. Somaroo Patel & Mrs. Chirauji Devi and my family member's for their love, affection, prayer and support.*

*I am thankful to non-teaching staff of Department of Chemistry, Indian Institute of technology, Banaras Hindu University, Varanasi.*

*I am also thankful to MHRD for providing financial assistance during my research work.*

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# ABBREVIATIONS USED

$\eta\%$ = Percentage of inhibition efficiency

$C_R$ = Corrosion rate ($mgcm^{-2}h^{-1}$)

$C_R^o$ = Corrosion rate in uninhibited system ($mgcm^{-2}h^{-1}$)

$C_R^i$ = Corrosion rate in inhibited system ($mgcm^{-2}h^{-1}$)

E.W. = Equivalent weight of mild steel

$D$ = Density of metal ($g\ cm^{-3}$)

$Q$ = magnitude of the CPE ($\Omega^{-1}\ s^n\ cm^{-2}$)

$j$ = imaginary unit ( $\sqrt{-1}$ )

$\omega$ = angular frequency ($2\pi f$, $f$ the frequency)

$f$ = Frequency of component of impedance ($s^{-1}$)

$C_{dl}$ = Double layer capacitance ($\mu F\ cm^{-2}$)

$R_s$ = Solution resistance ($\Omega\ cm^2$)

$R_t^o$ = charge transfer resistance in absence of inhibitor ($\Omega\ cm^2$)

$R_t^i$ = charge transfer resistance in presence of inhibitor ($\Omega\ cm^2$)

$I_{corr}^o$ = Corrosion current density in uninhibited solution ($mA\ cm^{-2}$)

$I_{corr}^i$ = Corrosion current density in inhibited solution ($mA\ cm^{-2}$)

$E_{corr}$ = Corrosion potential (mV/SCE)

$\beta_a$= Anodic Tafel constant ( $mVdec^{-1}$)

$\beta_c$= Cathodic Tafel constant ( $mVdec^{-1}$)

$\lambda$ = Arrhenius pre-exponential factor (mg $cm^{-2}$ $h^{-1}$)

$E_a$ = Activation energy (kJ $mol^{-1}$)

$R$ = Universal gas constant (J $K^{-1}$ $mol^{-1}$)

$T$ = Absolute temperature (K)

$N$ = Avogadro's number ($6.023 \times 10^{23}$ $mol^{-1}$)

$h$ = Planck's constant (J-s)

$K_{ads}$ = Adsorption equilibrium constant ($M^{-1}$)

$\Delta G°_{ads}$ = Gibbs free energy of adsorption (kJ $mol^{-1}$)

$\theta$ = Degree of surface coverage of metal

$C_{inh}$ = Concentration of inhibitor (mol $L^{-1}$, ppm)

$E_{HOMO}$ = Energy of highest occupied molecular orbital

$E_{LUMO}$ = Energy of lowest unoccupied molecular orbital

$\Delta E_{L\text{-}H}$ = Energy gap between HOMO and LUMO

$\Delta N$ = Number of electron transferred

$\Delta E_{MBG}$ = Singlet-triplet molecular band gap

$\chi_{Fe}$ = Electronegativity of iron

$\chi_{inh}$ = Electronegativity of inhibitor

$\eta_{Fe}$ = Hardness of iron

$\eta_{inh}$ = Hardness of inhibitor

$\Delta N$ =Fraction of electron transfer

$IP$ = Vertical ionization potential of inhibitor

$EA$ = Vertical electron affinity of inhibitor

$\Delta E_T$ = Total energy transfer after inhibitor adsorption

$E_{total}$ = Sum of energies of inhibitor molecule and metallic surface

$E_{Fe\ surface}$ = Energy of metallic surface before inhibitor adsorption

$E_{molecule}$ = Energy of the inhibitor molecule before adsorption of inhibitor molecules

$E_{interaction}$ = Interaction energy between metal surface and inhibitor molecules

$E_{ads}$ = Adsorption energy.

# PREFACE

Corrosion is a phenomenon of universal interest; it is degradation of materials particularly metals and alloys by electrochemical interaction with the environment. Corrosion can be very expensive as well as unsafe due to failures of various kinds and the need for expensive replacements which may occur even though the amount of metal destroyed is quite small. Due to increased use of metals and alloys in all fields of science and technology and increased pollution of air and water which generates more corrosive environments, the knowledge of corrosion and its prevention has become necessary. The annual global cost of corrosion was estimated to be around $ US 2.5 trillion which constitute about 3% of the world GDP. However, the cost of corrosion can be reduced about 20-25% by applying recently available methods of corrosion prevention. Nowadays, the corrosion inhibitors is being used as the most popular and effective technique for combating corrosion. As the title itself reflects, the thesis highlights the attempts made in developing heterocyclic compounds such as 5-arylpyrimido-[4, 5-b] quinoline-diones, 2-amino-4-arylquinoline-3-carbonitriles, 2, 4-diamino-5-(phenylthio)-5H-chromeno [2, 3-b] pyridine-3-carbonitriles and 3-amino alkylated indoles as corrosion inhibitors.

The thesis starts with introduction highlighting the technological and economic significance of the problems associated with corrosion. The various forms and theories of corrosion have been described in order to explain the mechanism of corrosion. In the later part of the introduction, different measures of metallic corrosion inhibition with particular emphasis of heterocyclic compounds as corrosion inhibitors in acid solution have been described. The literature on the metallic corrosion inhibition by heterocyclic compounds as corrosion inhibitors

has been surveyed. The results obtained from the gravimetric and electrochemical techniques have been discussed section wise in terms of several commonly used corrosion parameters such as percentage inhibition efficiency ($\eta$%), corrosion rate ($C_R$), charge transfer resistance ($R_{ct}$), corrosion current ($i_{corr}$) and corrosion potential ($E_{corr}$). The activation and thermodynamic parameters have also been calculated in order to find mechanistic information about the adsorption of inhibitor molecules on the metallic surface. The effects of inhibitors concentration and solution temperature on inhibition efficiency of the heterocyclic compounds have also been discussed. The SEM, EDX and AFM studies have been employed to confirm the presence of protective film of inhibitors on the mild steel surface. The DFT based quantum chemical calculations and molecular dynamics simulations have been carried out in order to correlate experimentally determined inhibition efficiencies with several computed parameters such as energy of highest occupied and lowest unoccupied molecular orbitals, $E_{HOMO}$ and $E_{LUMO}$, respectively, energy band gap ($\Delta E$), global hardness ($\eta$) and softness ($\rho$), electronegativity ($\chi$), fraction of electron transfer ($\Delta N$) and dipole moment ($\mu$). A possible mechanism of corrosion has been proposed on the basis of experimental and computational analysis.

Major part of the thesis has been published in *RSC Advances* 6 (2016) 15639-15654, *RSC Advances* 5 (104), 85417-85430, *RSC Advances* 6 (2016) 53933-53948, *and Journal of Molecular Liquids* 219 (2016) 647-660.